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**ADHESIVE THERMOPLASTIC
COPOLYMERS
FOR THE
WIRE AND CABLE INDUSTRY**

G. E. Clock, G. A. Klumb, R. C. Mildner

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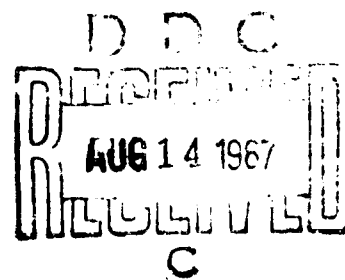
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ADHESIVE THERMOPLASTIC COPOLYMERS FOR THE WIRE AND CABLE INDUSTRY

by

G. E. Clock, G. A. Klumb, and R. C. Mildner

INTRODUCTION:

Adhesive layers have always played a limited role in cable construction. The mechanical weakness of the earlier natural materials, such as bitumens and waxes, limited their functions to corrosion protection and moisture barriers. The crosslinked and synthetic bonding agents, which later became available to the industry, required heat treatments sufficiently complicated to limit their application to special cases. A new family of thermoplastic copolymers has been developed. These offer for the first time adhesive polymers with good structural properties. The high bonding strength of these polymers to a variety of substrates suggests many interesting possibilities for new cable constructions.

CHARACTERISTICS OF THE ADHESIVE COPOLYMERS:

Their Chemical Nature:

These copolymers consist of a backbone essentially polyethylenic in form with attached carboxyl groups. By variation of these two components, the physical properties can be varied over a wide range. It is, therefore, possible to meet the requirements of a number of widely differing applications. For example, polymers with either the general physical properties of low density polyethylene with its good ductility and easier processing or the characteristics of linear polyethylene with higher heat distortion and better abrasion resistance can be obtained by employing the proper backbone. Since the properties of low density polyethylene meet the requirements of most cable applications, the emphasis of this paper is on the low density version.

Variation in the amount of comonomer will change those properties of the polymer which denote toughness and adhesion. Figure 1 shows the change in ultimate tensile strength with increase in comonomer level. With increasing comonomer, the tensile strength increases very rapidly to a little over 4,000 psi. Thus, through the incorporation of comonomer, we are able to have the strength of linear polyethylene with the processing ease and other general properties of low density polyethylene. The results of the dart drop impact test are shown in Figure 2. This test measures

the resistance of a film to puncture and is a good indication of toughness. Again, a very rapid rise in toughness is noted with increasing levels of comonomer. The high values obtained indicate the tough, rubberiness of these copolymer films.

The most significant property resulting from the addition of comonomer is adhesion. While straight polyethylene is a waxy material, very difficult to bond, the copolymer will bond to a number of substrates. Figure 3 shows the bond strengths obtained between aluminum and steel with resins containing various amounts of comonomer. Bond strength data obtained on copper, lead and tinplate steel give values in the same range as those in Figure 3. The adhesive characteristics will be discussed in greater detail later in the paper.

Another property improvement of importance is in the greater stress crack resistance of these copolymers. Figure 4 shows the changes in stress crack resistance as the amount of comonomer is increased. Figure 4 and Table I indicate that stress crack resistance of the copolymers is not as dependent on melt index as with straight polyethylene homopolymers.

Properties essentially unaffected by variations in the comonomer ratio are elongation, hardness and yield strength.

Let us examine one resin called Experimental Resin QX-2375 which appears to offer a good balance of physical properties. The general physical properties of this resin are compared to a commercial low density homopolymer in Table II and Table III. A significant increase in tensile strength, as noted earlier, and an improved toughness as shown by tensile impact will be noted. Other than a slightly poorer WVTR and slightly greater power factor, the good properties of polyethylenes are retained.

Since polymers used in the wire and cable industry may have to operate over a wide range of environmental conditions, we have included data on several properties over a wide temperature range. In Figure 5 the improved tensile strength of the QX-2375 copolymer is shown to be maintained over a wide range of temperatures. In Figure 6 the high elongation measured at the low temperature is indicative of the improved low temperature brittleness over straight homopolymer.

By far, the most important property contributed by the addition of the reactive carboxyl groups is adhesion. When properly applied, these polymers will adhere to a great variety of substrates. Excellent adhesion has been obtained to most metals,

steel, tinsplate steel, aluminum, copper and lead, to celluloseics such as paper and wood, to glass and to several polymeric resins, e.g., epoxy, nylon, polyurethane. A special pretreatment technique is required to obtain adhesion to most other polymers. The good adhesion of certain inks to the surface of the copolymer without the need of pretreatment is also significant.

To obtain a good bond, it is only necessary that the adhesive copolymer wet the surface of the substrate. To do this, the polymer must be in a sufficiently fluid state and under enough pressure to cause it to contact the substrate. The adhesive strength of the bond is relatively insensitive to laminating pressure or time providing the surface is thoroughly contacted.

No rigorous cleaning procedures are required. Surprisingly, excellent bonds have been obtained to metal surfaces contaminated with oil.

We have been successful in continuously coating both light and heavy gauge aluminum and steel coil stock with this polymer. Coating thicknesses down to 1/4 mil have been applied with good adhesion.

Bond strength data of both the QX-2375 and the linear copolymer called QX-4262.6 have been measured over a wide temperature range. Figures 7 and 8 give these data on both peel and shear type failures.

Stability:

These copolymers unformulated are less stable to high temperature and conditions of outdoor exposure than homopolymers. This is probably due to the reactivity of the pendant carboxyl groups. However, properly formulated, these copolymers approach regular polyethylene in stability.

The addition of small amounts of carbon black will greatly improve the weatherability as it does with regular polyethylene. This loading does not seriously impair the adhesion to a metallic substrate. Additional studies have shown that copolymer containing even higher carbon black loading in the range of 30 to 50 per cent by weight still have good adhesion.

Availability of Material:

Several copolymers covering a range of comonomer levels and melt indexes are available in granular form in commercial quantities. Limited quantities of these resins containing carbon black can be obtained for experimental use.

Fine powders of these resins have been made in developmental quantities and are available for selected sampling. These can be applied by powder spray gun or fluidized bed techniques.

Coil stock of aluminum and tinplate steel have been extrusion-coated with various thicknesses of these resins on equipment available in our company. Samples of coated metal can be made available for evaluation.

Electrical Properties:

The carboxylic groups present lead to a small increase in dielectric constant at low frequencies, the magnitude of which is proportional to the comonomer content. The dielectric constant and dissipation factor of QX-2375 over a wide range of frequency are shown in Figure 9. The characteristics are not significantly affected by prolonged immersion in water.

POTENTIAL APPLICATIONS TO THE CABLE INDUSTRY:

The previous section has indicated the great versatility of this range of copolymers, both in regard to the range of properties that can be made available and to the manner in which the material can be incorporated in normal cable making processes. It can be applied as an extruded covering over polyethylene or over a metal shield so as to become effectively bonded to the substrate. Foils or laminates can be applied as a cable wrapping in helical or longitudinal form and bonded to a neighboring element either by a subsequent extrusion or by a simple heat treatment. It can be applied as a powder either in a fluidized bed or sprayed from a gun and consolidated by subsequent heating. It is also possible to deposit the resin from a solution in solvents such as xylene. Rather than consider specific applications to cable design, which is the province of the cable engineer, it seems best to review the special property of the construction which can be improved by the use of these resins. It will usually be found that more than one property is enhanced in any given construction. We believe that careful design can lead to worthwhile savings in weight of materials used which in many cases will more than offset the cost of providing the resin coating.

Reduced Moisture Permeation:

All organic materials have a finite moisture vapor transmission coefficient which, even with the most suitable materials, is sufficiently high to prevent their use in certain circumstances. Thus, if hygroscopic material or air-spaced constructions form part of the insulation of the cable, it is usually necessary to

see that the cable jacket provides an hermetic seal, in the form of a seamless lead or aluminum sheath or a welded-seam metal covering. By bonding a thin metal tape shield to a plastic jacket, it is possible to reduce the cross-section and to increase the length of path through which the moisture can permeate and thereby reduce by several orders of magnitude the amount of moisture that can enter the cable within its normal life. A number of alternative constructions may be used: the jacket itself may be the copolymer resin or alternatively a conventional material may be used for the jacket which is bonded to metal substrate. In the latter case, the metal tape may be laminated with the adhesive resin or alternatively the formed tape shield may be lapped with a copolymer resin foil which becomes bonded to the metal and to the jacket by the heat of extrusion.

Adhesive copolymers may be used, in place of soldering or butt-welding, to seal an overlapped or flanged joint in metal shields formed by folding a longitudinal plain or corrugated metal tape. Adhesion of the plastic jacket can also be useful in reducing the hazards due to occasional pinholes in welded or soldered seams.

Improved Corrosion Resistance:

Continuous bonding of plastic material to a metal substrate will inhibit corrosion in environments of high humidity in cases where the metal would normally corrode in the presence of water and air. Bonding the jacket to the outside of the metal sheath will greatly reduce the danger of corrosion in the event the jacket is cut or punctured during installation or in service. Coating both sides of the metal sheath with the adherent coating will provide corrosion protection to the inside as well in case the sheath itself becomes punctured. In an attempt to demonstrate the corrosion resistance properties of the coating, the following tests were run:

Panels 4" x 12" of carbon steel, aluminum, copper and lead were coated both sides with approximately 3 mils of QX-2375. On one side of each panel a scribe in the form of a cross was cut through the coating exposing the metal. These panels were then placed into a chamber maintained at 100°F and approximately 100 per cent relative humidity. After 22 months' exposure, no corrosion was observed on any of the panels on the unscribed surface. On the scribed surface, the aluminum and lead were corroded only where the metal was exposed. No corrosion or loss of adhesion extended back from the scribe. The steel and copper panels corroded in the scribe and for about 1/8" under the film on either side of the scribe. In a further test where the steel was pretreated by bonderizing, corrosion did not extend beyond the scratched line.

Improved Mechanical Properties:

There are two cases where bonding may be used to impart greater toughness to the cable construction.

1. It is often considered desirable to use as thin a metallic covering as possible in the interests of lightness and economy. This trend is often carried to the extreme so that the thin cylindrical shields tend to be unstable when bent beyond a certain limiting radius: the metal may be stress-hardened at the kinked portion so that premature failure by cracking may occur with repeated bending or vibration. This danger is widely recognized and cable designers resort to corrugation of such shields for cables beyond a certain size; this in turn leads to a bulkier cable and the use of more jacketting material.

By bonding a relatively thick jacket to the folded thin-metal shield or to a thin extruded lead sheath, a substantial improvement is effected in the mechanical stability of the shield.

2. It is sometimes required to transmit mechanical tensions from the outside of the cable to the inner components which are often of higher tensile modulus and greater mechanical strength than the outermost parts. Such cases are encountered in pulling cable into difficult duct-lines or in the case of drop wire used with extended spans. In the past it has been usual to rely upon thermal shrinkage to obtain a compact construction which has the requisite friction between the various components. This is at best rather unsatisfactory because it is highly dependent upon critical process conditions and because the existence of adequate mechanical couplings can only be gauged by isolated tests of the cable ends. Bonding of the components by means of these adhesive resins provides a reliable solution to the problem with more adequate margin of safety.

Equally the toughness of the jacket is improved by being bonded to the metal substrate so that it is better able to withstand rough treatment and avoids the wrinkling and stripping of the jacket which is sometimes encountered when cables are pulled through ducts or along the ground.

The methods of bonding outlined earlier can often be used in the cases mentioned above. In the case of lead sheaths, an adhesive coating might be applied by passing the sheathed cable through a fluidized bed of QX-2375 powder as it passes from the press, consolidating the coating with radiant heat and then quenching the plastic coating before the cable is reeled on to a drum. A plastic jacket can be made to adhere to the coating through the heat of extrusion, combined perhaps with limited preheating of the coating.

A striking example of the mechanical improvement which is possible is illustrated in Figures 10 and 11. Three simulated cable samples with substantially the same dimensions were prepared. A polyethylene tube of 0.75" O. D. and 60 mils wall was wrapped with an aluminum/copolymer laminate, laid longitudinally with about 1/2" overlap: the thickness of the aluminum was 25 mils and that of the copolymer, which was on the outer side of the aluminum, was 4 mils. A second polyethylene tube, also of 60 mils wall, was fitted tightly around the assembly, the overall diameter being about 0.93". In sample A, the assembly was left unbonded and in sample B, the aluminum was bonded to the outer polyethylene tube by raising the temperature to 140°C over a period of 90 minutes and then cooling. In sample C a 2-mil copolymer film was inserted under the aluminum tape and the whole consolidated by a heat treatment similar to that given to sample B. The test involved bending the samples around a 10" diameter mandrel with a semi-circular groove of 1-1/16" diameter. Bending the cable, straightening it and then bending it in the reverse direction constitutes one complete bend.

Figure 10 shows an X-ray photograph of the 3 samples after one 1/2 bend: Sample A has kinked and collapsed whereas the other two samples are substantially undamaged. Figure 11 shows the position after 3-1/2 bends: Sample B shows continuous wrinkles over the inner side of the bend, whereas sample C is still superficially undamaged. Sample B showed slight signs of incipient wrinkles under X-ray after 2 bends but there was no obvious external indications of damage. A fourth sample, identical to sample C was subsequently subjected to repeated bends to failure. After 61-1/2 complete bends, both tube and metal fractured in one place with little distortion elsewhere as shown in Figure 12.

Improved Electrical Effects:

The bonding of electrical shields to the solid insulation will in many cases improve the stability of the cable characteristics by more closely defining the capacitance of the cable and by avoiding the free charges which are created by the separation of a metallic shield and a solid dielectric (the so-called microphony effect). In certain cases the electric breakdown strength may be

improved and the electrical losses reduced by eliminating air spaces at the dielectric boundary which may discharge at high electric stresses.

Conductive Joints Between Metal Foils:

In certain cases it may be desirable that metal shield should be bonded together conductively. This can be done by thinly sprinkling a hard brittle metal alloy powder between the two parts which have to be joined: one alloy which we have used for this purpose is Mg₁₇Al₂. If a somewhat lower conductance can be tolerated, a resistive plastic can be made by compounding the QX-2375 resin with, say, 50 phr. of a conducting carbon black such as Vulcan XC-72; we have been able to effect bonds having a specific resistance down to about 0.5 ohm.-cm², but it seems unwise to rely upon a value less than 50 ohm.-cm².

Applications in Cable Accessories:

1. Joint Filling Compounds

In the case of joint casing which are filled with bitumen or waxes which are solid at the operating temperature, adhesion to the walls of the casing is highly desirable. It has been found that the adhesion of bitumen to metals is vastly improved by the addition of up to 35 per cent of copolymers such as QX-2375.

2. Underwater Cable Glands:

There are a number of cable applications where cables have to be taken through a bulkhead or gland and have to withstand very high pressure differences under water. Such cases occur in submarine naval vessels and in the submerged repeaters of transoceanic telephone cables. Because of their importance to successful operation, it is possible to tolerate a bonding process which may be time consuming and elaborate. The metal surface must be cleaned and pretreated, in some cases electroplated, and then provided with an adherent polyethylene coating. The union between this coating and the cable core is then made by an injection molding. In order to maintain the necessary temperature control and cleanliness of the component parts, the assembly is desirably performed in conditions closer to the laboratory than the workshop. By contrast, the bonding between, for instance, polyethylene covered cores and brass or steel glands by means of the copolymer resins described here would

appear to be relatively straight-forward. Our experience indicates that it should be possible with a single injection molding process to secure adequate adhesion both to a heated metal gland and to the polyethylene core.

CONCLUSIONS:

We have given some of the pertinent characteristics of one particular copolymer in a range of new resins which by reason of their unique adhesive properties seem likely to have a marked influence on design in the cable industry, as they have in other fields. We have indicated in general terms how the resins may be used to modify existing designs to improve their general operating characteristics. Further, we believe that in many cases their use will lead to related economics in materials which will more than offset the cost of the coating material and any additional process that may be involved. It is not intended to suggest that their successful application can be made without careful experimental work because ~~we are~~ aware that in certain cases the solution to the heat transfer problem may be quite critical. Furthermore, it seems that some experimental work may prove necessary before the most economical designs, made possible by the use of these materials, are evolved.

TABLE I

STRESS CRACK RESISTANCE EXPERIMENTAL RESIN QX-2375

POLYMER		POLYETHYLENE TYPICAL L.D.		EXPERIMENTAL RESIN QX-2375			
STRESS CRACK RESISTANCE 168 HOURS *	MELT INDEX	.25	1.8	0.51	0.82	1.25	3.75
	100% IGEPAL	0/20	20/20	0/20	0/20	0/20	0/20
	100% HOSTAPAL H.L.	20/20	20/20	0/20	0/20	0/20	10/20 (81 hours)

* No failures in 20 samples within 168 hours

TABLE II

TYPICAL PHYSICAL PROPERTIES of EXPERIMENTAL RESIN QX-2375

PROPERTY	MEASURED AT 23°C.	
	CG-1705	QX-2375
MELT INDEX	5	5
DENSITY	.917	.934
TENSILE STRENGTH, psi	1365	3360
YIELD STRENGTH, psi	1360	1415
ELONGATION, %	585	595
LOW TEMP. BRITTLE POINT, °F.	-65°	<-70°
TENSILE IMPACT	1100	3500
RIGIDITY, psi	1.6×10^4	1.5×10^4
HARDNESS, SHORE C	80	85
SPENCER IMPACT (1.5 mils)	715	3310
DART DROP (1.5 mils)	70	682
POWER FACTOR (1 MEGACYCLES)	2×10^{-4}	15×10^{-4}
DIELECTRIC CONSTANT (1 MEGACYCLE)	2.28	2.30
WVTR, GMS./100 IN. 2/24 HRS. / MIL.	1.12	1.25

TABLE III
COMPARISON OF THE PHYSICAL PROPERTIES OF
JACKETTING STOCK *

PROPERTY		TEST METHOD ASTM	QX-2375.2 COPOLYMER	TYP. LOW DEN. P.E. COMPOUND
MELT INDEX		D1238	0.45	0.25
TENSILE STRENGTH, PSI		D412	3500	2165
YIELD STRESS, PSI		D412	1800	1485
ELONGATION, %		D412	580	560
LOW TEMP. BRITTLINESS POINT, °C.		D746	>-76	>-76
DENSITY		D1505	0.9485	0.931
HARDNESS		D676	D60	D54
STIFFNESS, PSI		D747	1.27×10^4	1.82×10^4
VICAT SOFTENING POINT, °C.		D1525	93	94
DIELECTRIC CONSTANT		D150	2.48	2.50
DISSIPATION FACTOR		D150	0.0043	0.0043
ENVIRONMENTAL STRESS CRACK RESISTANCE		MODIFIED [†] D1693		
FAILURES IN 168 HRS.	10% IGEPAL 100% IGEPAL 100% HOSTAPAL		0/20 0/20 0/20	10/20 (24 HRS.) 0/20 20/20 (8 HRS.)

* Loaded with 2.6 % Carbon Black for protection against UV

† Oven annealed. Slow cooling rate, 5 °C./hour

FIG. 1

TENSILE STRENGTH VS COMONOMER LEVEL

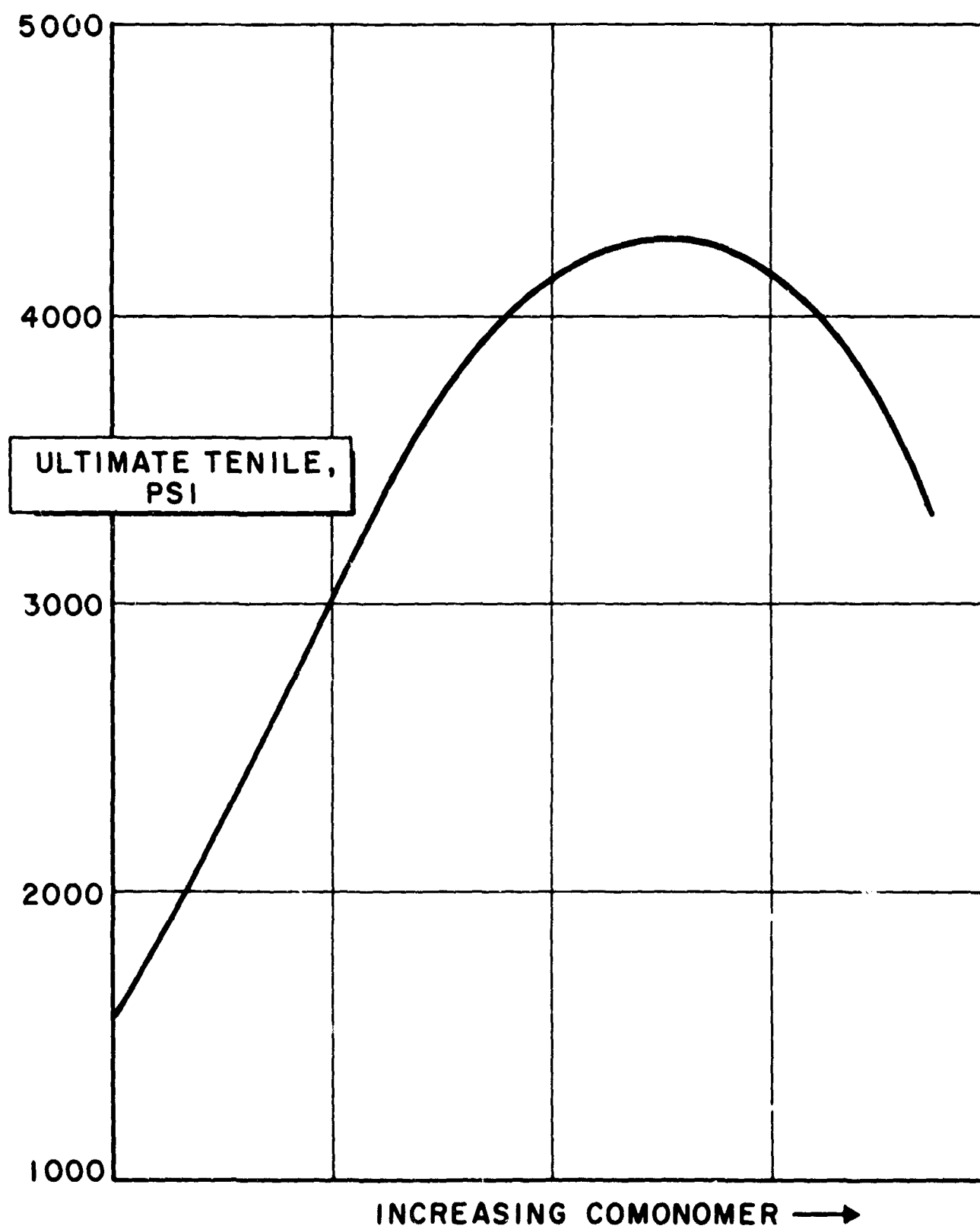


FIG. 2

DART DROP IMPACT VS COMONOMER LEVEL

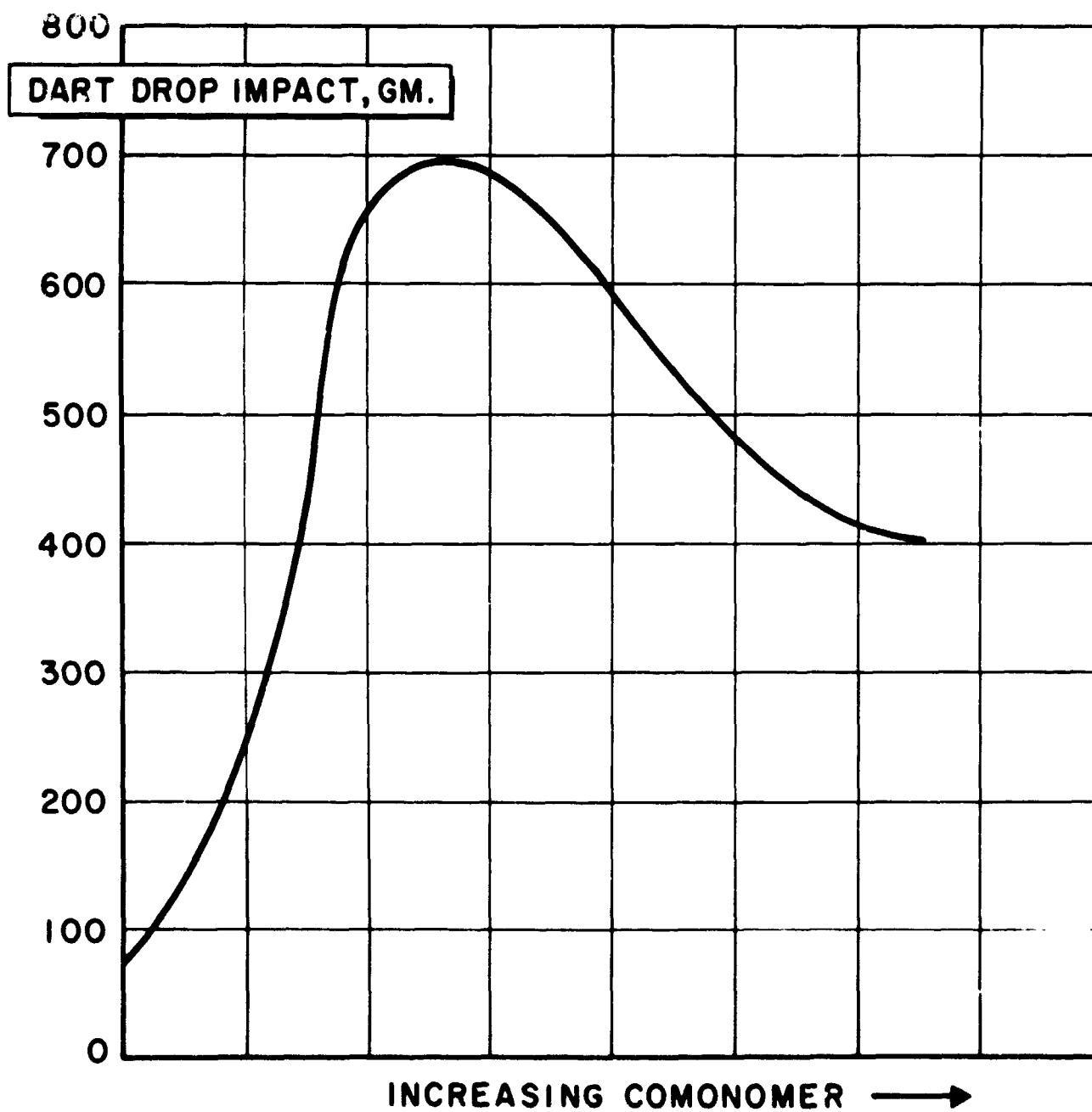


FIG. 3

ADHESION VS COMONOMER LEVEL

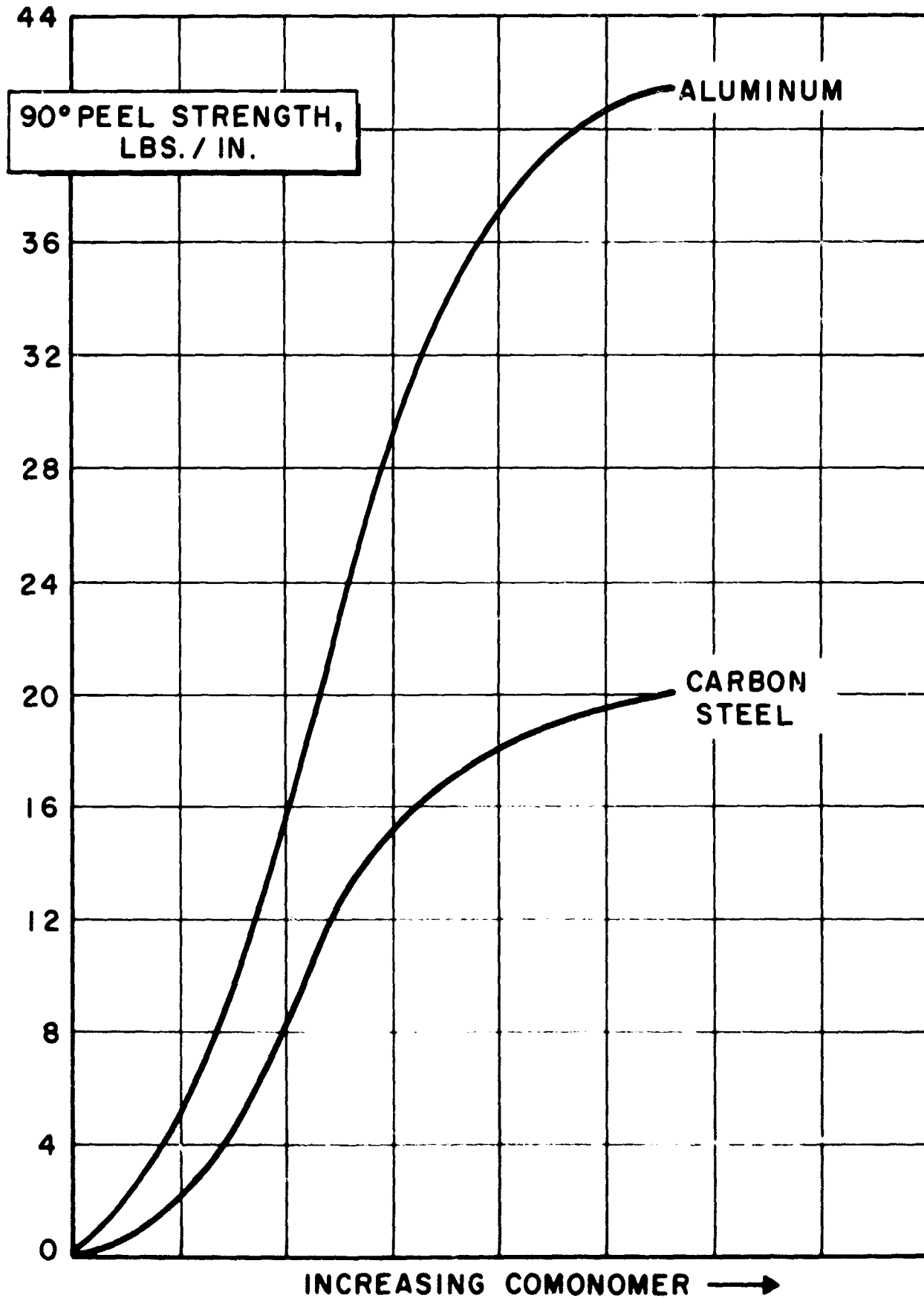


FIG. 4

**STRESS CRACK RESISTANCE
VS
COMONOMER LEVEL**

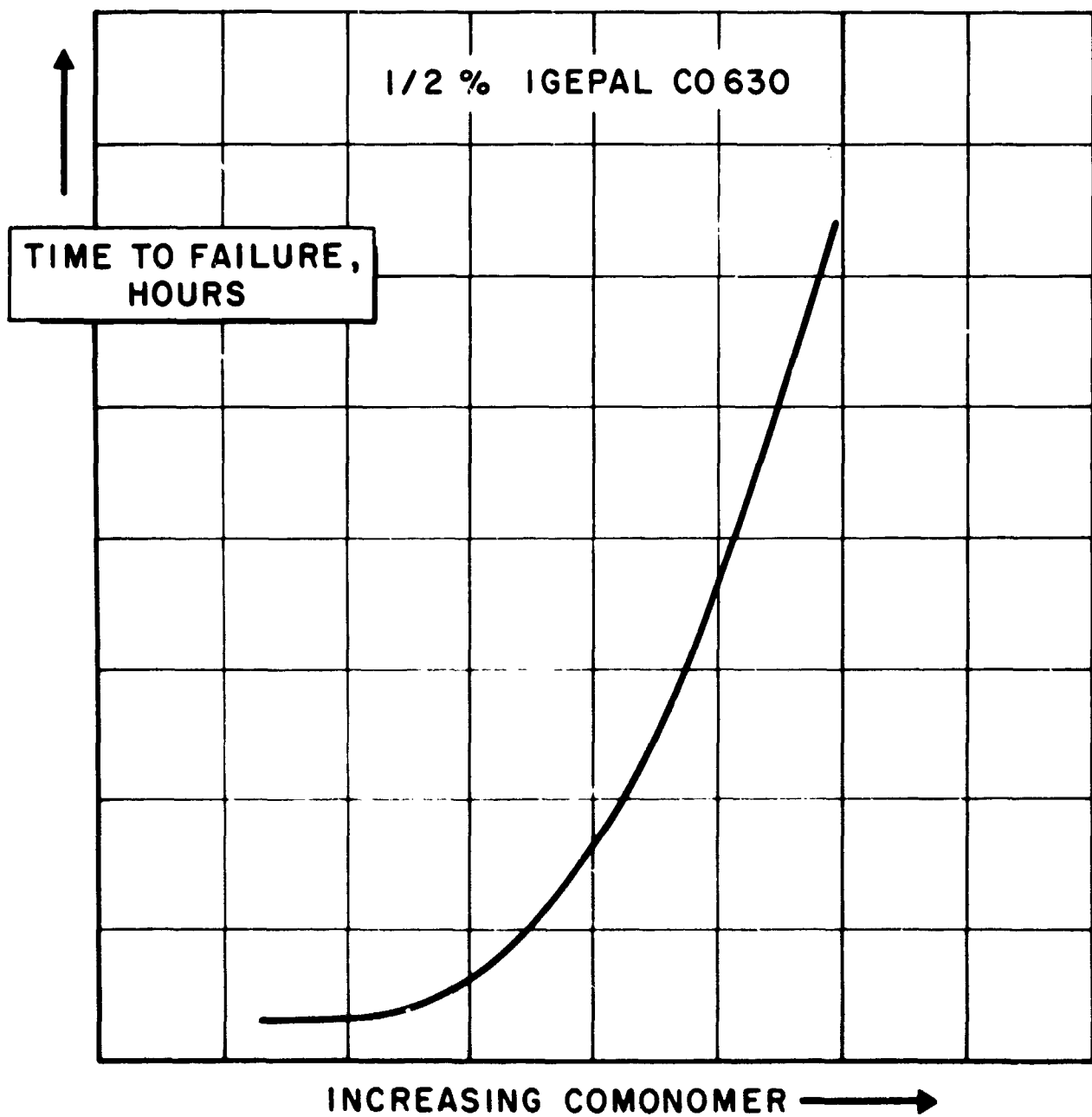


FIG. 5

TENSILE STRENGTH VS TEMPERATURE

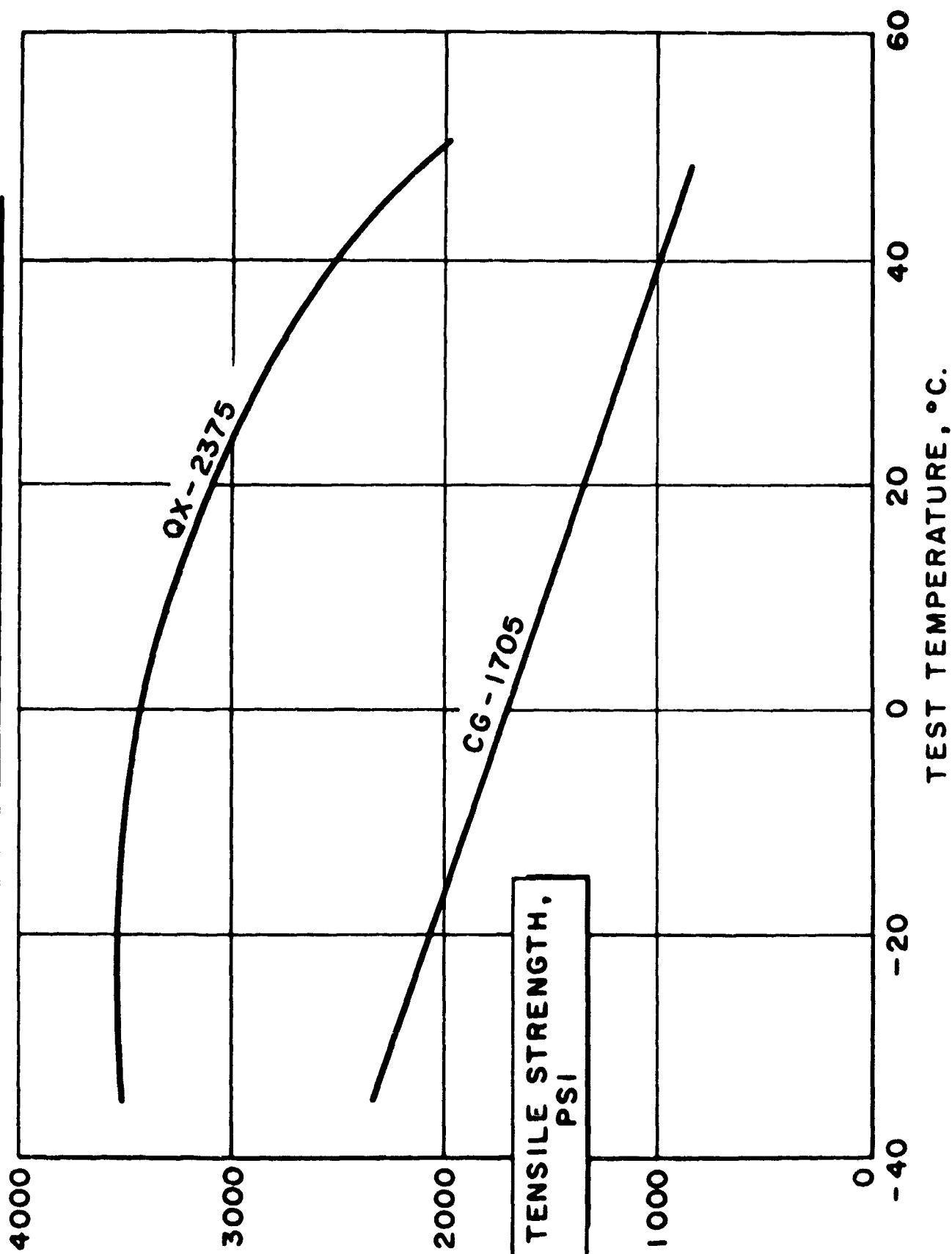


FIG. 6

ELONGATION (AT BREAK) VS TEMPERATURE

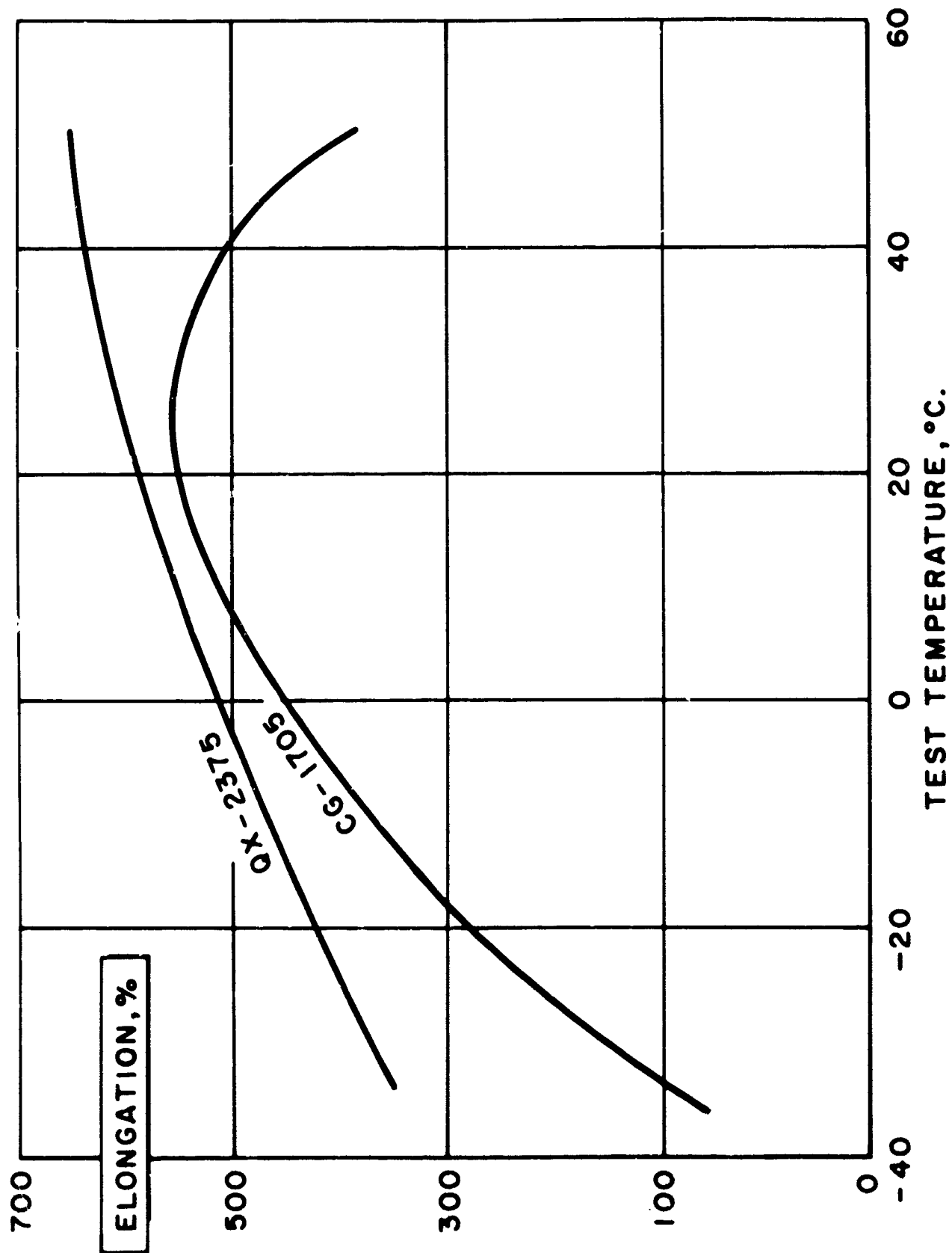


FIG. 7
Al ADHESION-180° Metal Peel 6 mil Al VS TEMP.

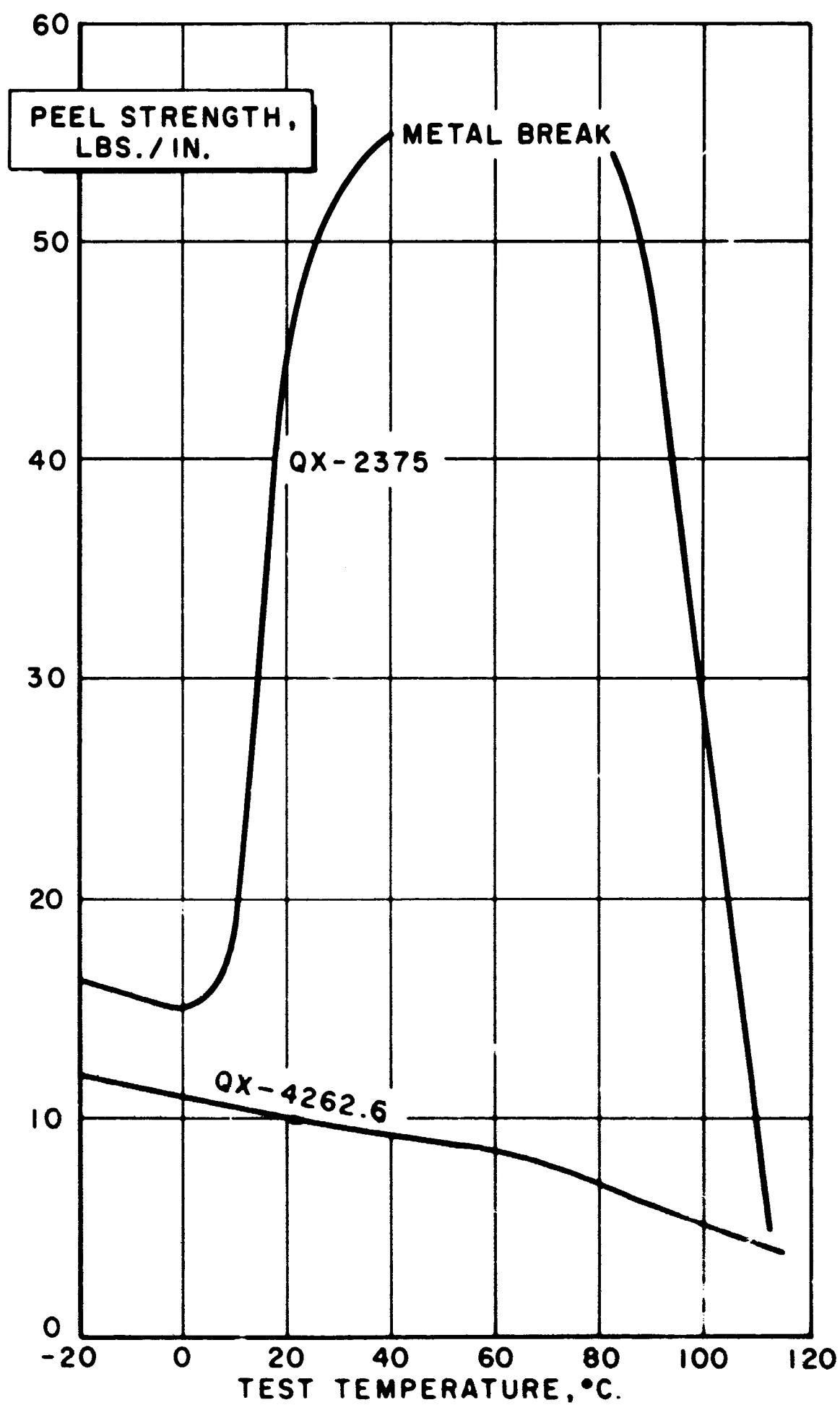


FIG. 8

AI ADHESION-LAP SHEAR VS TEMPERATURE

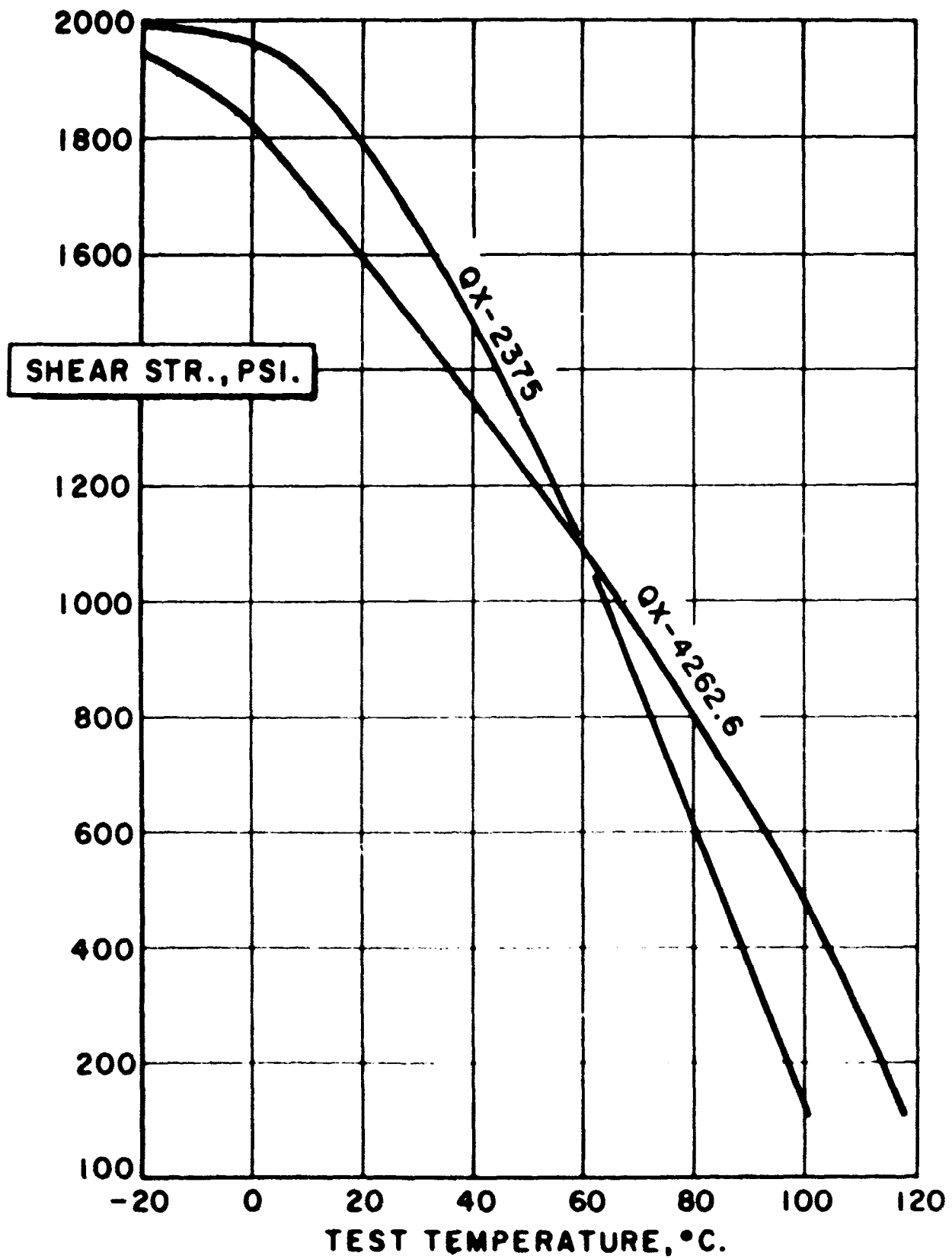


FIG. 9

ELECTRICAL PROPERTIES EXPERIMENTAL RESIN QX-2375

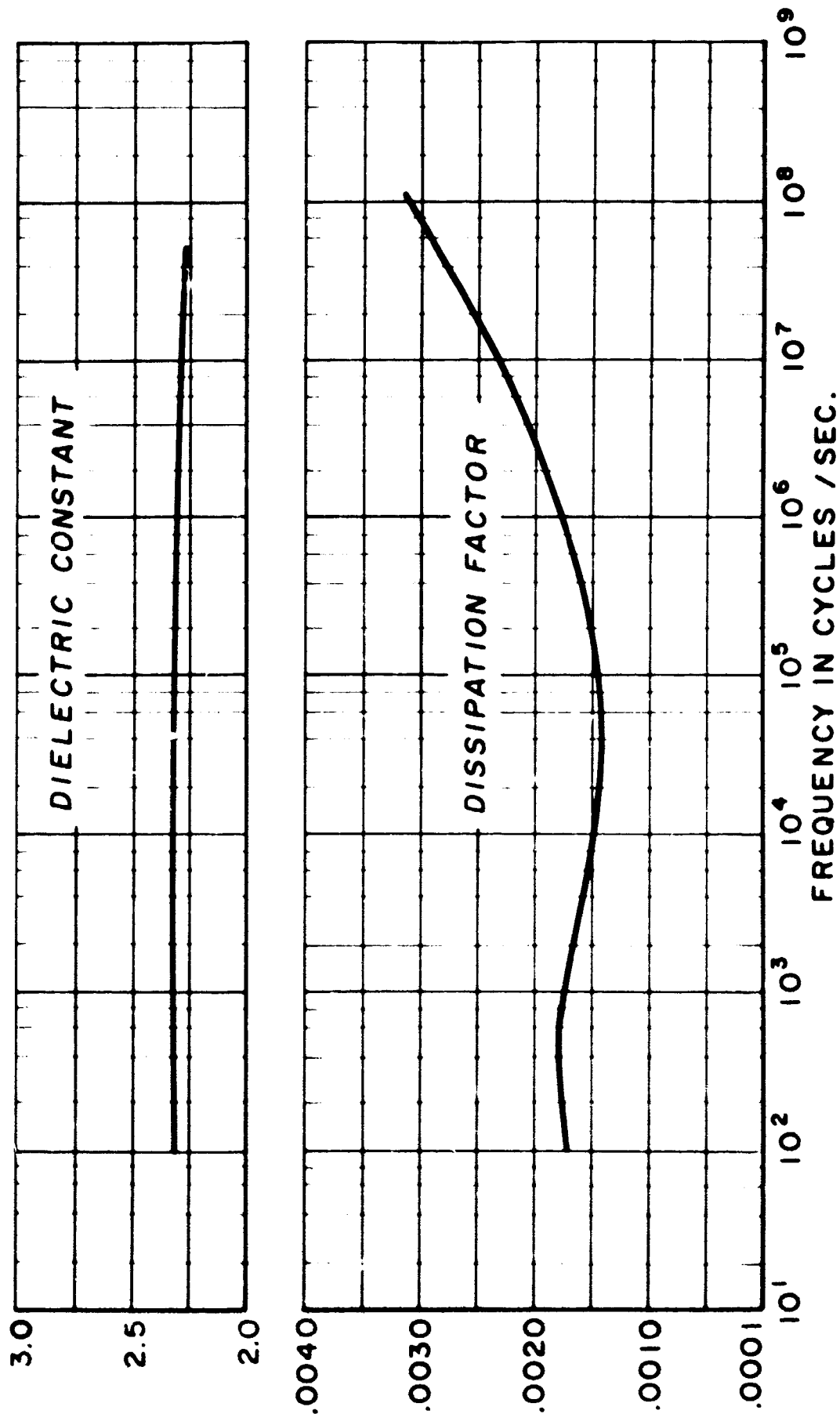


Figure 10

X-RAY PHOTOGRAPHS OF SIMULATED CABLE SAMPLES AFTER 1/2 BEND (10" Mandrel)

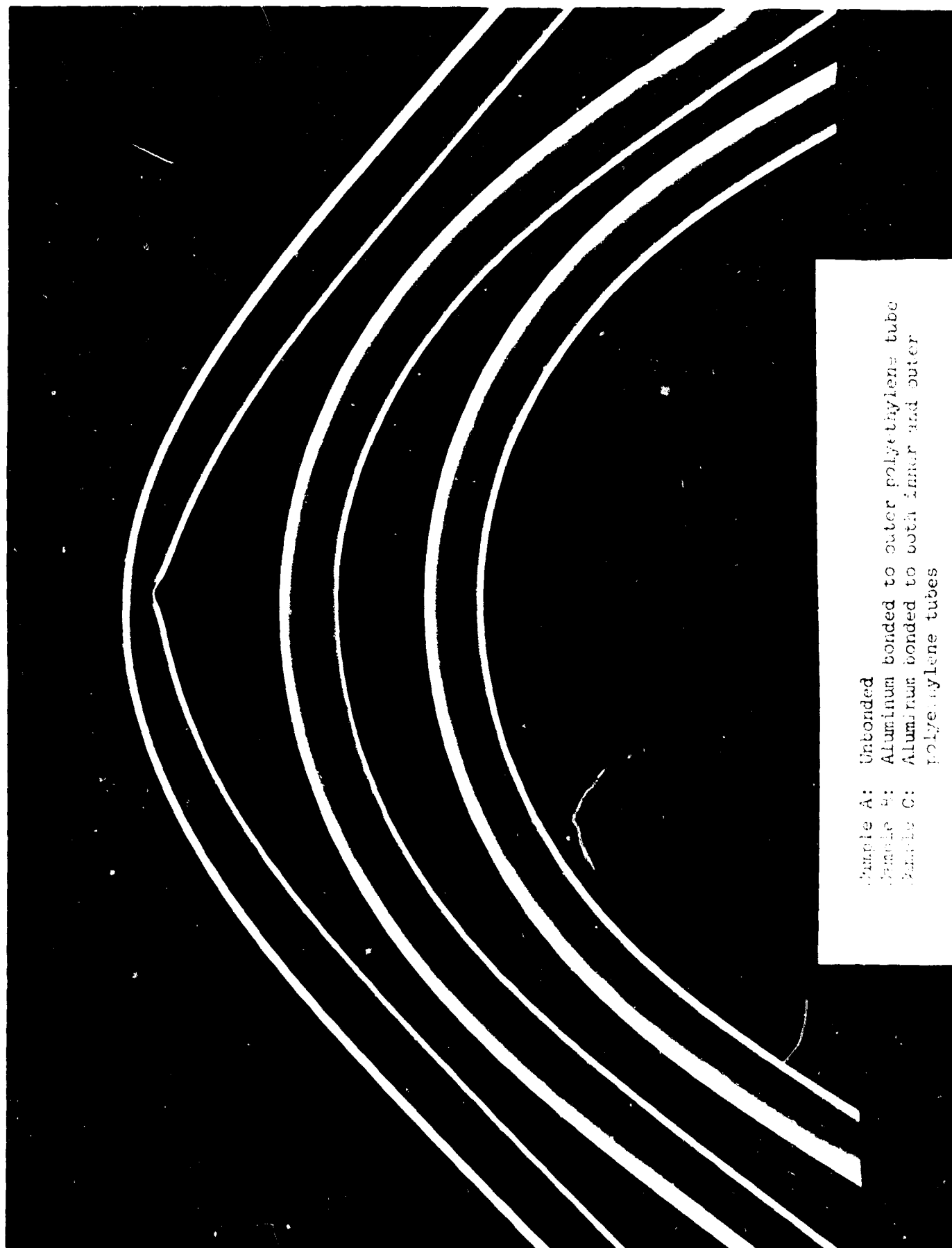
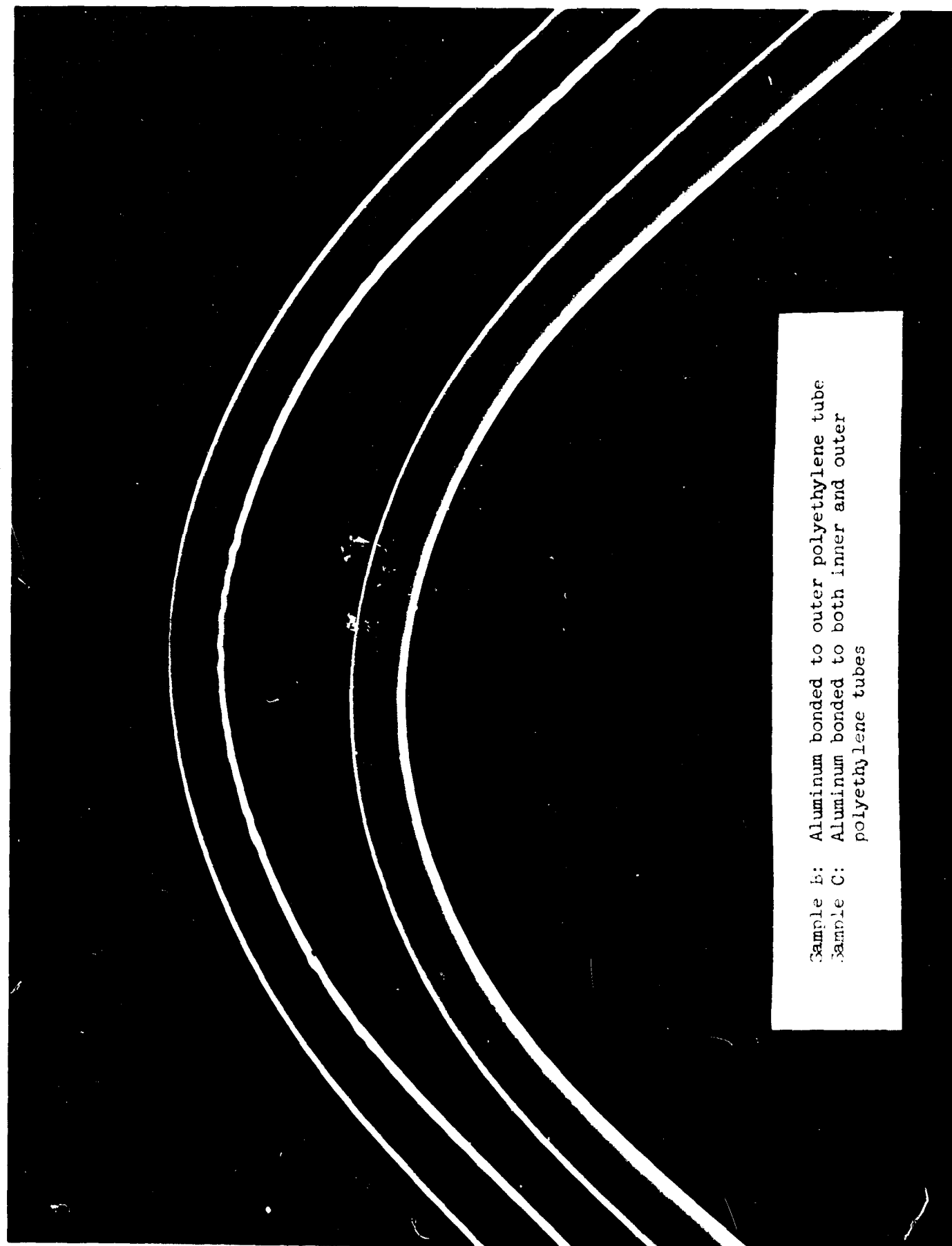


Figure 11

γ-RAY PHOTOGRAPHS OF SIMULATED CABLE SAMPLES AFTER 3-1/2 BENDS (10" Mandrel)



A high-contrast, black and white photograph of a circular, heavily textured object, possibly a metal disc or a piece of wood, held by a dark, curved support structure. The object shows significant wear, including scratches and a central hole. The background is white.

They will be all coming around to both inner and outer space by way of the